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【Title of Invention in Korean】 열산 발생제를 포함하는 포토레지스트 조성물을 이용하여 포토레지스트 패턴 폭 감소 현상을 개선하는 방법

【Title of Invention in English】 Pattern width slimming-inhibiting method of photoresist pattern using photoresist composition containing thermal acid generator

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【Objective】 The above Application was filed in accordance with Republic of Korea Patent Law Article 42.

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【Fees】

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【Additional Fee】	0 Pages	0 won
【Priority Document Fee】	0 Case	0 won
【Request for Examination Fee】	0 Claims	0 won
【Total Fee】		29,000 won

【Attached Document】 1. Abstract, Specification (and Drawing): 1 copy each

[ABSTRACT]

[Abstract]

A pattern width slimming-inhibiting method of photoresist pattern using photoresist composition containing thermal acid generator. When the formed pattern is heated, a thermal generator generates acid during the heating process, and a cross-linking reaction occurs to photoresist compositions, thereby preventing pattern width slimming due to SEM-beam for CD measurement.

[Representative Figure]

Fig. 2B

[SPECIFICATION]

[TITLE OF THE INVENTION]

PATTERN WIDTH SLIMMING-INHIBITING METHOD OF PHOTORESIST PATTERN USING PHOTORESIST COMPOSITION CONTAINING THERMAL ACID GENERATOR

[BRIEF DESCRIPTION OF THE DRAWINGS]

<1> Figure 1A is a photograph of a photoresist pattern obtained according to a conventional method that is taken immediately after the CD measurement using a SEM.

<2> Figure 1B is a photograph of a photoresist pattern obtained according to the conventional method that is taken after approximately thirty seconds since the CD measurement using the SEM.

<3> Figure 2A is a photograph of a photoresist pattern obtained according to the present invention that is taken immediately after the CD measurement using the SEM.

<4> Figure 2B is a photograph of a photoresist pattern obtained according to the present invention that is taken after approximately thirty seconds since the CD measurement using the SEM.

[DETAILED DESCRIPTION OF THE INVENTION]

[OBJECTS OF THE INVENTION]

[FIELD OF THE INVENTION AND BACKGROUND ARTS]

<5> A method for inhibiting pattern width slimming or reduction of photoresists is disclosed. In particular, a method for inhibiting pattern width slimming due to the beam emitted by a scanning electron microscope (hereinafter, it is abbreviated to "SEM") while measuring a critical dimension (hereinafter, it is abbreviated to "CD") of a photoresist pattern obtained by using a photoresist composition comprising thermal acid generator is disclosed.

<6> Typically, the semiconductor processing is carried out by setting up a CD target and the SEM measures the CD when a photoresist pattern is formed. When the CD is measured immediately after a pattern is formed, the CD is almost identical with a target. However, thirty seconds after the CD measurement by the SEM, that is, during the observation by the SEM, width of the pattern gets slimmed. The basic mechanism of the SEM is that image is seen through e-beam projected under high vacuum. Most of the ArF photoresist gets cracked due to e-beam and at that time, the cracked parts are disappeared due to high vacuum, which consequently slims pattern width. Therefore, there were many problems in establishing the CD target during a semiconductor processing because measuring the CD itself is very difficult.

<7> The present inventors completed the present invention by finding that the above-mentioned problems could be solved by adding thermal acid generator into the photoresist compositions.

[TECHNICAL ACHIEVEMENT OF THE INVENTION]

<8> An object of the present invention is to provide a method for preventing a photoresist pattern from being slimming while measuring its CD using SEM after photoresist pattern formation.

[Configuration of the Invention]

<9> To accomplish the above object, the present invention provides pattern width slimming-inhibiting method of photoresist pattern using photoresist composition containing thermal acid generator.

<10> Hereinafter, the present invention is described in more detail.

<11> First, the present invention provides a method of pattern formation improving pattern width slimming-inhibition of photoresist pattern by using photoresist composition containing thermal acid generator.

<12> The method of pattern formation is comprising the steps of:

<13> (a) coating a photoresist composition containing a thermal acid generator on a substrate to form a photoresist film;

<14> (b) exposing the photoresist film;

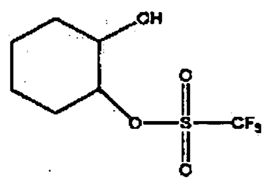
<15> (c) developing the exposed photoresist film to obtain a photoresist pattern; and

<16> (d) heating the photoresist pattern.

<17> The photoresist composition includes a thermal acid generator, chemically amplified photoresist resin, a photoacid generator and organic solvent.

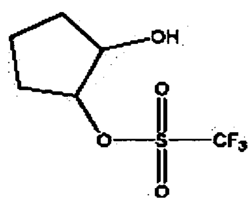
<18> Some of preferred thermal acid generators are disclosed, but are not limited to, as following Formulas 1 to 4:

<19> Formula 1



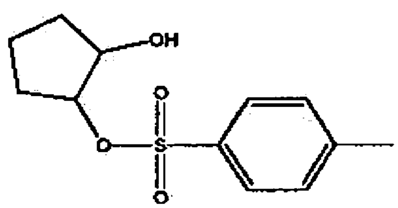
<20>

<21> Formula 2



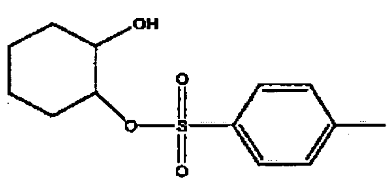
<22>

<23> Formula 3



<24>

<25> Formula 4



<26>

<27> Meanwhile, as for the chemically amplified photoresist resin of the present invention, cyclo olefin repeating unit having hydroxyalkyl functional group is employed in order to form a cross-linking bond and to improve adhesiveness to the substrate. And cyclo olefin repeating unit having carboxyl functional group or maleic

anhydride repeating unit can be further included in the photoresist resin. In addition, the photoresist resin should not flow at about 150°C or higher, the point where the thermal acid generator begins to release an acid. Preferred photoresist polymer is poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride).

<28> The thermal acid generator is generally used in an amount of ranging from about 0.1 to about 5 wt% based on that of the photoresist resin employed.

<29> In addition, any of conventional photoacid generator, which is able to generate acids when it is exposed to light can be used. Preferably, the photoacid generator is diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenyl triflate, diphenyl p-toluenyl triflate, diphenyl p-isobutylphenyl triflate, dibutylnaphthylsulfonium triflate or mixture thereof. Preferred organic solvent for photoresist composition is propyleneglycol methyl ether acetate, propyleneglycol methyl ether, ethyl lactate, methyl 3-methoxypropionate, ethyl 3-ethoxypriopionate or cyclohexanone, etc.

<30> In the step (b), exemplary light sources which are useful for forming the photoresist pattern include EUV (Extreme Ultra Violet), VUV (Vacuum Ultra Violet;157nm), ArF(193nm), KrF(248nm), E-beam, X-ray or ion beam. The process for forming the photoresist pattern can further include a soft baking which is performed before the step (b) and/or a post baking which is performed after the step (b). Preferably, the soft and post baking steps are performed at temperature of around

110°C. As long as the temperature does not exceed 150°C, no acid is generated from the thermal acid generator during the soft baking or post baking process.

<31> Preferably, the heating step (d) is carried out at a temperature higher than 150°C, where a thermal acid generator begins to release an acid, and more preferably, at a temperature range from about 150 to about 250°C.

<32> In contrast to the conventional method for forming a photoresist pattern, an additional step of heating the formed pattern is carried out, in which acid is generated by a thermal acid generator. The produced acid catalyzes cross-linking reaction, between hydroxyl group and carboxyl group; hydroxyl group and maleic anhydride; or carboxyl group and maleic anhydride in photoresist resins.

<33> Another embodiment provides a semiconductor element that is manufactured using the photoresist composition described above.

<34> The disclosed methods will now be described in more detail by referring to the examples below, which are not intended to be limiting.

<35> <u>Comparative Example</u>

<36> To 7.2g of PGMEA (propylene glycol methyl ether acetate) solvent was added 1g of poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride) and 0.012g of triphenylsulfonium triflate, and the resultant was filtered to obtain a photoresist composition.

<37> The photoresist composition was coated on the silicon wafer, baked at 110 °C for 90 seconds and exposed to light using ArF laser exposing device. The

photoresist composition was post-baked at 110 °C for 90 seconds, and developed in 2.38 wt% aqueous TMAH solution to obtain a 138nm L/S pattern right after measuring the CD of the pattern using the SEM (see Fig. 1A). Thirty seconds after the measurement by the SEM, the pattern was slimmed by 26nm, that is the pattern became 112nm L/S pattern (see Fig. 1B).

<38> <u>Invention Example</u>

<39> To 7.2g of PGMEA (propylene glycol methyl ether acetate) solvent was added 1g of poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride), 0.012g of triphenylsulfonium triflate, and 0.2g of a thermal acid generator of Formula 2, and the resultant was filtered to obtain a photoresist composition.

<40> The photoresist composition was coated on the silicon wafer, baked at 110 °C for 90 seconds and exposed to light using ArF laser exposing device. The photoresist composition was post-baked at 110 °C for 90 seconds, and developed in 2.38 wt% aqueous TMAH solution to obtain a 138nm L/S pattern right after measuring the CD of the pattern using the SEM (see Fig. 2A). The formed pattern was heated at 175 °C for 60 seconds and the CD was measured by using the SEM. At this time, no slimming occurred and 138nm L/S pattern was maintained (see Fig. 2B).

<41> As described above, according to the conventional method, the CD measurement using the SEM during a semiconductor processing was almost impossible due to the slimmed pattern as much as 26nm. However, according to the

present invention, the pattern after the CD measurement did not get slimmed, thus a semiconductor processing was proceeded regardless of the CD measurement.

[EFFECT OF THE INVENTION]

<42> As shown above, when a photoresist composition containing a thermal acid generator is employed for a photoresist pattern forming process and additionally the resultant pattern is heated after developing step, a cross-linking reaction occurs to patterning photoresist compositions, and the SEM-beam has no effect on the patterns, which consequently makes it easy to set up the CD target during the semiconductor process.

[CLAIMS]

[Claim 1]

A process for forming a photoresist pattern comprising the steps:

(a) coating the photoresist composition comprising a thermal acid generator on a substrate to form a photoresist film;

(b) exposing the photoresist film;

(c) developing the exposed photoresist film to obtain a photoresist pattern; and

(d) heating the photoresist pattern.

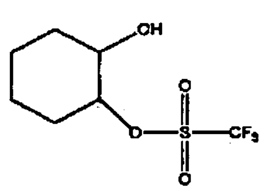
[Claim 2]

The process according to claim 1, wherein the photoresist composition comprises a thermal acid generator, a chemically amplified photoresist resin, a photoacid generator, and an organic solvent.

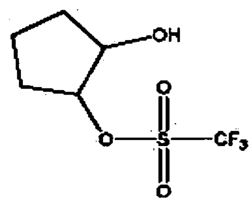
[Claim 3]

The process according to claim 1, wherein the thermal acid generator is selected from the group consisting of compounds of the Formulas 1 to 4:

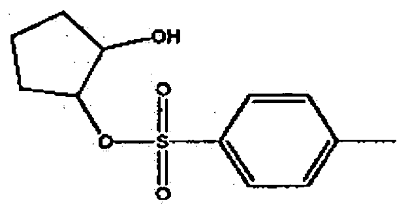
Formula 1



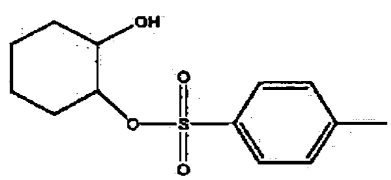
Formula 2



Formula 3



Formula 4



[Claim 4]

The process according to claim 2, wherein the chemically amplified photoresist resin further comprises more than one repeating unit selected from the group consisting of cyclo olefin repeating unit having a carboxyl group and maleic anhydride repeating unit.

[Claim 5]

The process according to claim 4, wherein the photoresist resin is poly(tert-butyl bicyclo[2.2.1]hept-5-ene-2-carboxylate / 2-hydroxyethyl bicyclo[2.2.1]hept-5-

ene-2-carboxylate / bicyclo[2.2.1]hept-5-ene-2-carboxylic acid / maleic anhydride).

[Claim 6]

The process according to claim 2, wherein the thermal acid generator is used in an amount of 0.1 to 5 % by weight of the photoresist resin.

[Claim 7]

The process according to claim 1, wherein the exposing step (b) is carried out by using a light source selected from the group consisting of EUV (Extreme Ultra Violet), VUV (Vacuum Ultra Violet), ArF, KrF, E-beam, X-ray and ion beam.

[Claim 8]

The process according to claim 1, wherein the heating step (d) is carried out at a temperature of the thermal acid generator releasing an acid.

[Claim 9]

The process according to claim 8, wherein the temperature ranges from 150 to 250°C.

[Claim 10]

A semiconductor element manufactured by the process of claim 1.